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MEASUREMENT OF ATMOSPHERIC SULFATES:
EVALUATION OF THE METHYLTHYMOL BLUE METHOD

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ANALYSIS OF ATMOSPHERIC SULFATES:
EVALUATION OF THE
METHYLENE BLUE METHOD



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FOREWORD

This program, "Measurement of Atmospheric Sulfates: Evaluation of the Methylthymol Blue Method," is being conducted under the Environmental Protection Agency (EPA) Contract No. 68-02-1728, which is Midwest Research Institute (MRI) Project No. 3948-C. The program is concerned with methods for analyzing the water soluble sulfates in ambient air samples. The objectives of the program were (a) to conduct a thorough literature survey, (b) to select the two most promising methods, and (c) to subject the two methods to a ruggedness test.

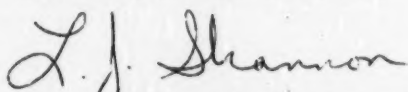
This is the final report of Phase III covering the ruggedness test of the methylthymol blue procedure. Included as an appendix is a new write-up of the method for sulfate analysis.

This program has as a requirement the submission of two final reports for Phase III; one for each of two methods evaluated during the program. The final report covering the evaluation of the second method is being submitted separately.

This program is being conducted under the management of Mr. Paul C. Constant, Jr., Head, Environmental Measurements Section of MRI's Physical Sciences Division. The principal investigator is Mr. Fred J. Bergman. He was assisted in the experimental investigation by Mr. William H. Maxwell. The statistical analysis was performed by Mr. Michael C. Sharp.

Approved for:

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April 2, 1976

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SUMMARY

The methylthymol blue (MTB) procedure used by EPA for sulfate analysis has been subjected to a ruggedness test. The method write-up has been modified to strengthen the procedure where required. A new procedure developed by EPA for extracting sulfates from the filter samples has been incorporated in the write-up. The absorbance for the MTB procedure has been established as hyperbolic. The method, as now presented, appears to be reasonably rugged with the exception of phosphate interference, which remains a problem. A potential approach for eliminating the phosphate interference is presented.

I. INTRODUCTION

Recent health effects studies have shown that the concentration of sulfate in ambient air presents a significant hazard to human health. The use of catalytic control devices in automobiles will possibly increase the level of atmospheric sulfate.

This has led to an increasing emphasis on the measurement of sulfate concentrations in ambient air. Since the data obtained may subsequently be used to set an ambient air standard for sulfates and may influence automotive standards for other emissions, it is important that the analytical methods used for sulfate analysis be reliable.

Establishing the reliability of analytical methods is the responsibility of the Environmental Monitoring and Support Laboratory of the Environmental Protection Agency. One method of accomplishing this is to subject candidate methods to a ruggedness test as described by W. J. Youden and Stow and Mayer.* The results of a ruggedness test then permits strengthening the methods and enables EPA to recommend the most reliable of the methods evaluated.

The program for accomplishing the above goals was divided into three phases. Phase I included a thorough literature search and an evaluation of the various methods with a recommendation of the two most promising methods. Phase II covers a familiarization period and a detailed method write-up for the two methods. Phase II includes the ruggedness test design and investigation and a qualitative identification of the significant and nonsignificant effects. This report presents a complete description of the familiarization phase and ruggedness test of the methylthymol blue (MTB) method of sulfate analysis. An MTB method write-up which incorporates the results of the ruggedness test and editorial comments by EPA is shown in the Appendix.

II. RESEARCH PROGRAM

During Phase I of this program, it became apparent that it would be desirable to select the MTB method as one of the two methods for evaluation. This selection was based on the following considerations: (a) the

* Statistical Techniques for Collaborative Tests, by W. J. Youden; AOAC Publication, Box 540, Benjamin Franklin Station, Washington, D.C. 20044, and "Efficient Screening of Process Variables," by R. A. Stowe and R. P. Mayer, Ind. Eng. Chem., 58:36-40 (1966).

method is well developed; (b) the National Air Surveillance Network (NASN) is presently using the method; (c) there are a number of organizations familiar with the procedure; (d) the method is automated, which permits a large number of samples to be run; (e) the method appears to produce acceptable results; (f) the results of the familiarization and ruggedness test can be applied to the method to strengthen it; and (g) most of the current sulfate investigators are employing the MTB method, making a comparison with a possible alternate highly desirable.

The literature search shows 13 references associated with the MTB method. Lingemen^{1/} presents a general description of automated analytical procedures from a clinical standpoint but does not describe a sulfate method. Körbl and Pribil^{2-7/} report the development and investigation of methylthymol blue as a metallochromic indicator. The remaining references^{8-13/} describe the automated MTB method first reported by Lazrus.^{8/} The two papers by Lazrus^{8,9/} and the procedure used by Morgan^{10/} were the same. Bostrom^{11/} recommended the use of silicon tubing for the reagent's lines but otherwise did not change Lazrus' method. There were slight differences between Lazrus', the Technicon, and the NASN method. They are summarized in Table 1.

TABLE 1

VARIATION IN REAGENT OPERATING PARAMETERS

	<u>Lazrus</u>	<u>Technicon II</u>	<u>NASN</u>
Sample, flow rate, ml/min	1.2	0.1	0.8
MTB flow rate, ml/min	1.2	0.7	1.2
Sample stream air flow rate, ml/min	0.8	0.32	0.23
Water flow rate, ml/min		2.0	1.4
NaOH flow rate, ml/min	0.6	0.42	1.0
Reagent stream air flow rate	0.6	0.32	1.0
meq. of HCl/min	0.0048	0.0028	0.0048
meq. of NaOH/min	0.06	0.076	0.15
Sample dilution	None	1:21	1:2-3/4
Total flow/BaSO ₄ prec.	2.4	2.8	2.8
Total flow/NaOH phase	1.8	2.92	3.0
meq. HCl/ml sol.	0.002	0.001	0.0017
meq. NaOH/ml sol.	0.033	0.026	0.05

The sample is diluted with water in two of the methods to change the range. The only other significant reagent changes in the methods were the amounts of HCl and NaOH added.

The physical operating parameters are shown in Table 2.

TABLE 2

PHYSICAL OPERATING PARAMETERS

	<u>Lazrus</u>	<u>Technicon</u>	<u>NASN</u>
Sample rate	30/hr	30/hr	30/hr
Concentration range µg/ml	0.5-50	0-300	5-60
Precipitation delay coil Length	120 in. ^{8/} 240 in. ^{9/}	43 in.	27 in.
Sample/wash	Not specified	6:1	1:2
Color development coil Length	8 in.	40 in.	27 in.
Wavelength	480 nm ^{8/} 465 nm ^{9/}	460 nm	460 nm

It was desirable to investigate all of the significant variations in the procedure to determine their effects.

A. Calibration Curve

The least defined part of the MTB method appeared to be the calibration procedure. It is generally agreed that a calibration plot does not follow the Beer-Lambert law. Lazrus' observation was that the plot was slightly concave. Other investigators have reported the curve to be either a power function, or in some cases, linear. This disagreement was considered to be one of the more important aspects to be investigated in evaluating the method.

A Technicon I Autoanalyzer module was assembled following the specifications given in the NASN procedure. Standards were prepared following the same procedure and then they were analyzed. Various concentrations were run in ascending, descending, and random orders. The peak height appeared to be representative of the sample analyzed and not influenced by large shifts in concentration either before or after a specific peak. The results of this analysis produced over 1,000 calibration points. Random data was subject to a least squares curve fit of six curves.

Of the six curves, the best fit was obtained with a linear function, $Y = A + (B \cdot X)$; a power function $Y = A \cdot X^B$; and a hyperbolic function $Y = X/(A + BX)$. The index of determination (square of the correlation coefficient or r^2) was always greater than 0.9 for these three curves and less than 0.9 for the other three. The index of determination of seven typical curves fits is shown in Table 3.

TABLE 3

INDEX OF DETERMINATION (r^2)

<u>Linear Function</u>	<u>Power Function</u>	<u>Hyperbolic Function</u>
0.991039	0.997017	0.99838
0.976019	0.990774	0.99662
0.970671	0.992314	0.998299
0.955881	0.988047	0.998266
0.957649	0.989792	0.999408
0.97526	0.993453	0.999411
0.978717	0.996125	0.999777

Although r^2 varies from run to run, the best fit is always obtained with the hyperbolic function $Y = X/(A + BX)$ followed by the power function and then the linear function.

The values obtained from a least squares curve fit using typical data is shown in Table 4 which includes calculated values for constants A and B.

The values of A and B in Table 4 were then used to calculate peak heights and the percent error for each point using the three best curves. The results of this operation are shown in Table 5.

Table 5 presents a more complete view of the results. The best overall fit is obtained with the hyperbolic function $Y = X/(A + BX)$. The power function fits slightly better at low values (peak height < 20) but does not equal the hyperbolic at midrange and high range. The linear function is inferior to both the hyperbolic and power function.

This evaluation confirms that the calibration curve is nonlinear and indicates that a hyperbolic function $Y = X/(A + BX)$ is optimum for the calculations.

TABLE 4

LEAST SQUARES CURVE FIT

<u>Curve Type</u>		Index of Determination <u>(r^2)</u>	<u>A</u>	<u>B</u>
Linear	$Y = A + (B \cdot X)$	0.991039	5.67479	2.58614
Exponential	$Y = A \cdot \text{Exp}(B \cdot X)$	0.890888	17.8936	4.50122E-2
Power	$Y = A \cdot X^B$	0.997017	3.43963	0.942017
Hyperbolic	$Y = A + (B/X)$	0.755255	113.005	-567.619
Hyperbolic	$Y = 1/(A + BX)$	0.707708	5.13178E-2	-1.06356E-3
Hyperbolic	$Y = X/(A + BX)$	0.99838	0.317611	1.16851E-3

Y = Peak height

X = SO_4^{--} Concentration in micrograms per milliliter

Values used were:

Y = 129.9,	X = 50
Y = 110.2,	X = 40
Y = 89.2,	X = 30
Y = 61.1,	X = 20
Y = 28.9,	X = 10
Y = 15.6,	X = 5

TABLE 5

CALCULATED VALUES AND PERCENT DIFFERENCE USING CONSTANTS
OBTAINED FROM A LEAST SQUARES CURVE FIT

Hyperbolic Function

<u>X-Actual</u>	<u>Y-Actual</u>	<u>Y-Calculated</u>	<u>Percent Difference</u>
50	129.9	132.966	-2.3
40	110.2	109.784	0.3
30	89.2	85.0661	4.8
20	61.1	58.6542	4.1
10	28.9	30.3678	-4.8
5	15.6	15.4581	0.9

Linear Function

<u>X-Actual</u>	<u>Y-Actual</u>	<u>Y-Calculated</u>	<u>Percent Difference</u>
50	129.9	134.982	-3.7
40	110.2	109.12	0.9
30	89.2	83.2589	7.1
20	61.1	57.3975	6.4
10	28.9	31.5362	-8.3
5	15.6	18.6055	-16.1

Power Function

<u>X-Actual</u>	<u>Y-Actual</u>	<u>Y-Calculated</u>	<u>Percent Difference</u>
50	129.9	137.079	-5.2
40	110.2	111.091	-0.8
30	89.2	84.7198	5.2
20	61.1	57.8234	5.6
10	28.9	30.0974	-3.9
5	15.6	15.6658	-0.4

B. Analytical Wavelength

Interference filters are normally available at 10-nm increments. To determine if the optimum wavelength filter had been selected, a scan was made of the systems absorbance. The results are shown in Figure 1. Curve A is of the barium chelate of MTB at a pH of 12.4. Curve B consists of the reagents at a pH of 2.8 prior to chelation. The wavelength of the spectrophotometer was checked prior to the analysis using a holmium glass reference standard.

It appears from an examination of the curve that the conversion to the chelate by pH adjustment is essentially complete. Less than complete conversion to the chelate would have been indicated by an absorption peak occurring at ≈ 435 nm on the A curve. This was not observed.

Spectrophotometric methods are normally performed using the wavelength where the absorption is at a maximum to obtain the greatest sensitivity. The MTB procedure produces a broad absorption curve. The exact analytically employed wavelength is therefore not critical. However, the analytical wavelength should be selected so that measurements are made near the maxima and within that portion of the curve where the slope is essentially zero.

If absorbance were to be measured where the slope of the curve is larger, a small change in the wavelength would produce a significant change in the absorbance. In the MTB procedure a change of 10 nm near the maxima (for example from 455 to 465) will produce a change of only 1% in the absorbance. A change of 10 nm where the slope is greater (for example from 500 to 510 nm) will produce a 3% change in the absorbance.

The absorbance curve indicates that any wavelength between 440 and 470 nm would meet the above criteria and that the normally employed 460-nm wavelength should be satisfactory.

C. Method Variables

In preparation for the ruggedness tests, a list of variables and test levels for the MTB method was compiled. This list is shown in Table 6. There are actually 27 functions listed in the table under 19 general classifications. The design of a ruggedness test for 27 functions was considered undesirable. Each function was therefore examined for its suitability for inclusion in the ruggedness test. If suitable, it was labeled yes under the heading Valid for Test. Those labeled no were reserved for individual evaluation and are discussed below.

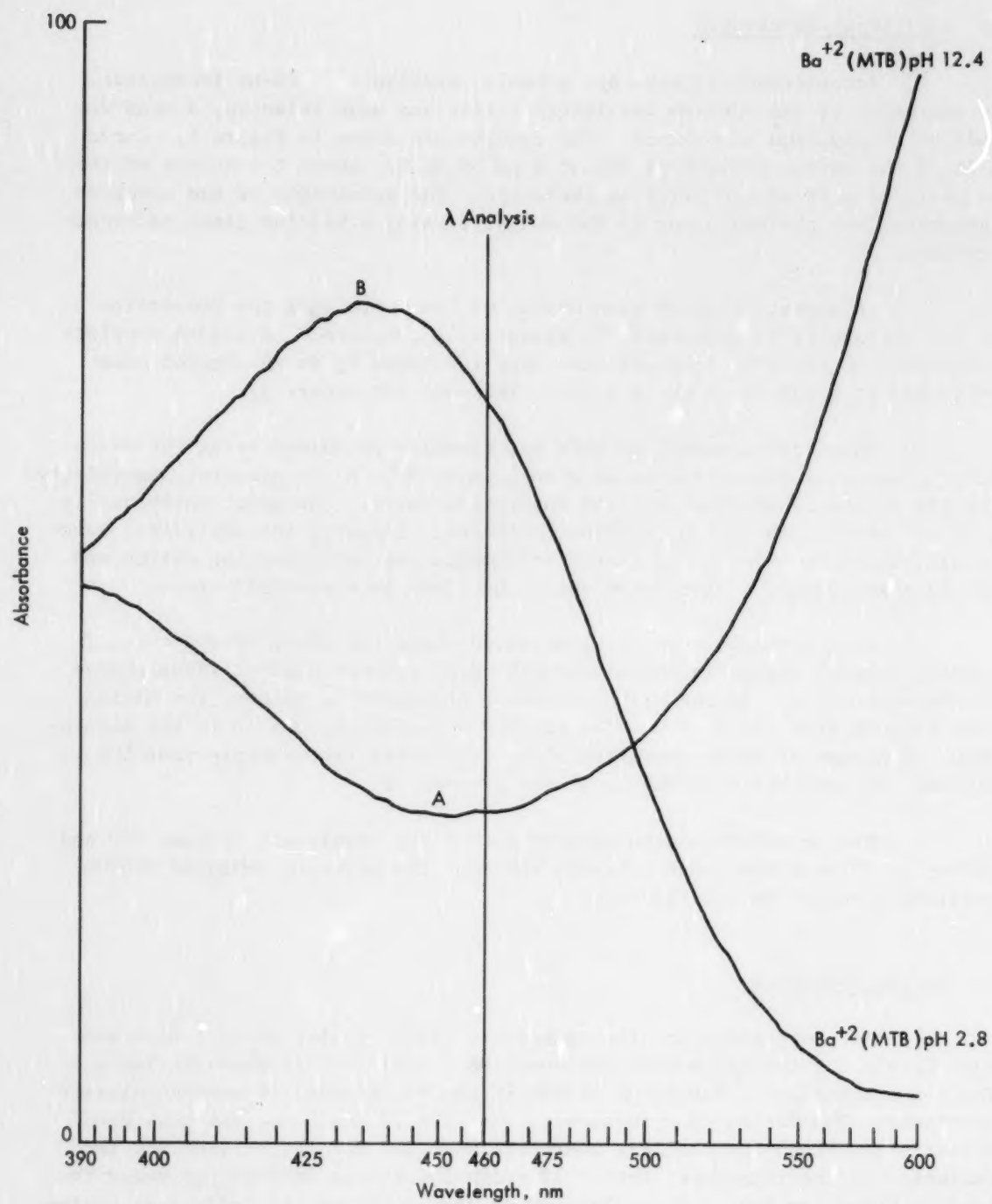


Figure 1 - MTB System Absorbance

TABLE 6
VARIABLES IN MTB METHOD

Function	Valid for Test	Levels	
		+	-
1. Ba/MTB ratio	Yes	1.00	0.90
Sample time	Yes	40	72
Wash time	Yes	80	108
2. MTB mixing time (coil)	No	29 turn	14 turn
3. NaOH color development time (coil)	No	29 turn	14 turn
4. Reagent age (stability) MTB	Yes	1 day	7 days
Sample age	No	1 day	14 days
5. Standard age (stability) (cold and dark)	No	1 day	14 days
6. Wash solution	No	EDTA	H ₂ O
7. Interferences			
Ba	Yes	0	30 µg
PO ₄	Yes	0	30 mg
Turbidity plus color	Yes	0	Filter ex- tract
S ⁼	No	0	30 µg
SO ₃ ⁼	No	0	30 µg
8. Concentration SO ₄ ⁼ (µg/ml)	Yes	30	120
9. Reaction temperature, MTB	Yes	20°C	30°C
10. pH, MTB solution	Yes	3.5	2.0
NaOH Reaction	Yes	13.5	12.0
11. Air in ion exchange column	No	Yes	No
12. Sample/water dilution	Yes	Yes	No
13. Pulse suppressor,			
MTB	No	Yes	No
NaOH	No	Yes	No
14. Air bubble rate, sample	Yes	0.23	0.32
MTB	Yes	0.32	1.00
15. Tubing materials	No	Si	Solv.
16. Ethanol concentration	Yes	400 ml	471 ml
17. Cations, 10 µg Fe + 10 Al + Ca	Yes	0	30 Total

D. Development Time

The analyzer was set up with a 29 turn coil inserted after MTB addition in place of the 3-in. (14 turn) coil specified in the method write-up. This allowed approximately double the normal time for barium sulfate precipitation. Three series of sulfate standards were then analyzed and the peak heights obtained were the same as those obtained with the 3-in. coil. The same procedure was followed in evaluating the color development time, again no change in the peak height was observed. It was therefore concluded that the coils specified in the method are satisfactory.

E. Reagent Stability

The stability of the MTB solution was included in the ruggedness test. The stability of the sample was given only a simple check. An ambient-air sample was extracted according to the method write-up. A portion of the extract was analyzed immediately and the remaining solution was stored in a volumetric flask in the laboratory ($\approx 22^{\circ}\text{C}$) for 14 days. The sulfate concentration remained unchanged.

A 30- $\mu\text{g}/\text{ml}$ standard sample was stored in a walk-in cooler (5°C in the dark) for 14 days. Analysis using a freshly prepared standard for calibration gave a value of 31 $\mu\text{g}/\text{ml}$ for the stored standard. The 30- $\mu\text{g}/\text{ml}$ standards stored cold and in the dark appear to be stable for at least 14 days. Other levels of sulfate standards were not checked.

F. Interferences

Interferences of major concern, based on earlier investigations, were evaluated. These consisted of phosphates, turbidity and color, and the cations Fe, Al, and Ca. The evaluation was conducted by including the interferences in the ruggedness test.

G. Air in the Ion Exchange Column

The inclusion of air bubbles in the ion exchange column appears to produce erratic results when the bubble is moving. Smaller bubbles (diameter less than that of the tubing that remains stationary) appears to have no effect. Since bubbles are removed from stream prior to entry in column, this is not normally a problem unless bubbles are accidentally admitted.

H. Pulse Suppressors

We could observe no effect on the precision or accuracy of the method related to the pulse suppressors in our system. Installing pulse suppressors made a slight improvement in the base line (decreased noise) but the precision was not significantly improved.

I. Tubing Materials

The analytical system was operated for extended periods of time with both Solvaflex and silicon pump tubing. No effect was observed other than the fact that the silicon pump tubing has a significantly longer life time. At present, silicon tubing appears to be good for at least 6 weeks of continuous daily operation.

J. Ruggedness Tests

The remaining functions listed in Table 6, which were not investigated individually, were evaluated using a ruggedness test. The test format is shown in Table 7. Most of the functions investigated are self-explanatory. The phosphate ion was investigated separately because of its known potential to cause an interference. Theoretically, the phosphate interference should be minimized since the precipitation is carried out at a pH of 2.8. The cations Fe, Al, and Ca were combined into a single function to simplify the ruggedness test. Color and turbidity were also combined for the same reason.

The format of Table 8 is technically a ruggedness test of dimension 20. The levels of the 19 variables are listed in Table 8.

The experimental design was the fractional framework given by Plackett and Burman (see Figure 2). However, the design did differ from an ordinary ruggedness test in that 12 replicate analyses per run were performed. In the normal ruggedness test (no replicates), the dummy "effects" are used as residual variance; this is quite conservative since the degrees of freedom are very small and the dummy effects contain interaction effects of the real variables (if any). The residual could also be estimated from the (pooled) replicate variance, although this is likely too liberal since the replicates are not experiment replicates but only analytical replicates.

The analysis of variance table is shown in Table 9. The response in this analysis is the difference between the actual sample value and the calculated value. In other words, the method bias is always used as the response (regardless of the level involved).

TABLE 7
SUCCEEDS TEST FOR METHYLTHIOHOL BLUE METHOD

Run No.	NaOH (g/500 ml)	NCL (ml/100 ml)	BaCl ₂ ·2H ₂ O (g/1000 ml)	MTB (g)	Ethanol (ml)	Sample Rate (cc/min)	Water Rate (cc/min)	Sample Air Rate (cc/min)	MTB Rate (cc/min)	MTB Air Rate (cc/min)	NaOH Rate (cc/min)	Analysis Temp. (°C)	MTB Age (days)	Sample Wash Time	PO ₄ (ug/ml)	Cations (Fe, Al, Ca) (ug/ml)	Color and Turbidity	Sample SO ₄ Concentration (ug/ml)	Dummy
1	+ 4.1	+ 9.0	- 1.4659	- 0.1301	+ 500	+ 1.00	+ 1.60	+ 0.32	- 1.20	+ 1.20	- 1.00	+ 35	- 0	- 40-80	- 0	- 0	+ Yes	+ 40	-
2	- 4.0	+ 9.0	+ 1.5000	- 0.1301	- 471	+ 1.00	+ 1.60	+ 0.32	+ 1.40	+ 1.00	+ 1.30	+ 25	+ 1	- 40-80	- 0	- 0	- No	+ 40	+
3	+ 4.1	- 8.3	+ 1.5000	+ 0.1400	- 471	- 0.80	+ 1.60	+ 0.32	+ 1.40	+ 1.20	- 1.00	+ 25	- 0	+ 72-108	- 0	- 0	- No	- 15	+
4	+ 4.1	+ 9.0	- 1.4659	+ 0.1400	+ 500	+ 1.00	- 1.60	- 0.32	+ 1.40	+ 1.20	+ 1.20	+ 25	+ 1	- 40-80	+ 30	- 0	- No	- 15	+
5	- 4.0	+ 9.0	+ 1.5000	- 0.1301	+ 500	+ 1.00	+ 1.60	+ 0.32	+ 1.40	+ 1.20	+ 1.20	+ 35	- 0	+ 72-108	- 0	+ 30	- No	- 15	-
6	- 4.0	- 8.3	+ 1.5000	+ 0.1400	- 971	+ 1.00	+ 1.60	+ 0.32	- 1.20	+ 1.20	+ 1.20	+ 35	+ 1	- 40-80	+ 30	- 0	+ Yes	- 15	-
7	- 4.0	- 8.3	- 1.4659	+ 0.1400	+ 500	- 0.80	+ 1.60	+ 0.32	- 1.20	+ 1.20	+ 1.20	+ 35	+ 1	+ 72-108	- 0	+ 30	- No	+ 40	+
8	- 4.0	- 8.3	- 1.4659	- 0.1301	+ 500	+ 1.00	+ 1.60	+ 0.32	+ 1.40	+ 1.20	- 1.00	+ 35	+ 1	+ 72-108	- 0	- 0	+ Yes	- 15	+
9	+ 4.1	+ 9.0	+ 1.5000	- 0.1301	- 471	+ 1.00	+ 1.60	+ 0.32	+ 1.40	+ 1.20	+ 1.20	+ 25	- 0	- 40-80	+ 30	+ 30	- No	+ 40	+
10	- 4.0	+ 9.0	- 1.4659	+ 0.1400	- 471	- 0.80	+ 1.60	+ 0.32	+ 1.40	+ 1.20	+ 1.20	+ 35	+ 1	+ 72-108	+ 30	+ 30	+ Yes	- 15	+
11	+ 4.1	- 8.3	+ 1.5000	- 0.1301	+ 500	+ 1.00	- 1.60	- 0.32	+ 1.40	+ 1.20	- 1.00	+ 35	+ 1	- 40-80	- 0	- 0	+ Yes	+ 40	+
12	- 4.0	+ 9.0	- 1.4659	+ 0.1400	- 471	- 0.80	+ 1.60	+ 0.32	+ 1.40	+ 1.20	+ 1.20	+ 35	+ 1	+ 72-108	+ 30	+ 30	+ Yes	- 15	+
13	+ 4.1	- 8.3	+ 1.5000	- 0.1301	+ 500	+ 1.00	- 1.60	- 0.32	- 1.20	+ 1.20	- 1.00	+ 35	+ 1	- 40-80	- 0	- 0	+ Yes	+ 40	+
14	+ 4.1	+ 9.0	- 1.4659	+ 0.1400	- 471	+ 1.00	+ 1.60	+ 0.32	- 1.20	+ 1.20	+ 1.20	+ 35	+ 1	+ 72-108	+ 30	- 0	- No	+ 40	+
15	+ 4.1	+ 9.0	+ 1.5000	- 0.1301	+ 500	- 0.80	+ 1.60	+ 0.32	- 1.20	+ 1.20	+ 1.20	+ 35	+ 1	+ 72-108	+ 30	+ 30	+ Yes	- 15	+
16	+ 4.1	+ 9.0	+ 1.5000	+ 0.1400	- 471	+ 1.00	+ 1.60	+ 0.32	- 1.20	+ 1.20	- 1.00	+ 35	+ 1	- 40-80	+ 30	+ 30	+ Yes	- 15	+
17	- 4.0	+ 9.0	- 1.4659	+ 0.1400	+ 500	- 0.80	+ 1.60	+ 0.32	+ 1.40	+ 1.20	- 1.00	+ 35	- 0	+ 72-108	+ 30	- 0	+ Yes	+ 40	+
18	- 4.0	- 8.3	+ 1.5000	+ 0.1400	+ 500	+ 1.00	- 1.60	+ 0.32	- 1.20	+ 1.20	+ 1.20	+ 25	- 0	- 40-80	+ 30	+ 30	- No	+ 40	+
19	+ 4.1	- 8.3	- 1.4659	+ 0.1400	+ 500	+ 1.00	+ 1.60	+ 0.32	+ 1.40	+ 1.20	+ 1.20	+ 25	- 0	- 40-80	- 0	- 0	+ Yes	- 15	+
20	- 4.0	- 8.3	- 1.4659	- 0.1301	- 471	- 0.80	- 1.60	- 0.23	- 1.20	- 1.00	- 1.00	- 25	- 0	- 40-80	- 0	- 0	- No	- 15	+

TABLE 8

RUGGEDNESS TEST OF DIMENSION 20

<u>Variable</u>	<u>Low Level (-)</u>	<u>High Level (+)</u>
A NaOH (g/500 ml)	4.0	4.1
B HCl (ml/100 ml)	8.3	9.0
C BaCl ₂ ·2H ₂ O (g/100 ml)	1.4659	1.5000
D MTB (g)	0.1301	0.1400
E Ethanol (ml)	471	500
F Sample rate (cc/min)	0.80	1.00
G Water rate (cc/min)	1.40	1.60
H Sample air rate (cc/min)	0.23	0.32
I MTB rate (cc/min)	1.20	1.60
J MTB air rate (cc/min)	1.00	1.20
K NaOH rate (cc/min)	1.00	1.20
L Analysis temperature (°C)	25	35
M MTB age (days)	0	1
N Wash/sample time	40/80	72/108
O PO ₄ (µg/ml)	0	30
P Cations (Fe, Al, Ca) (µg/ml)	0	30 of each
Q Color and turbidity	No	Yes
R Sample SO ₄ ⁼ concentrations (µg/ml)	15	40
S Dummy	-	-

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	
1	+	+			+	+	+	+		+		+					+	+		1
2	+			+	+	+	+		+		+					+	+		+	2
3			+	+	+	+		+		+					+	+		+	+	3
4		+	+	+	+		+		+					+	+		+	+		4
5	+	+	+	+		+		+					+	+		+	+			5
6	+	+	+		+		+					+	+		+	+			+	6
7	+	+		+		+					+	+		+	+			+	+	7
8	+		+		+					+	+		+	+			+	+	+	8
9		+		+					+	+		+	+			+	+	+	+	9
10	+		+					+	+		+	+			+	+	+	+		10
11		+					+	+		+	+			+	+	+	+		+	11
12	+					+	+		+	+			+	+	+	+		+		12
13				+	+			+	+			+	+	+	+		+		+	13
14				+	+		+	+			+	+	+	+		+		+		14
15			+	+		+	+			+	+	+	+		+		+			15
16		+	+		+	+			+	+	+	+		+		+				16
17	+	+		+	+			+	+	+	+		+		+					17
18	+		+	+			+	+	+	+		+		+					+	18
19		+	+			+	+	+	+		+		+				+	+		19
20																				20

+ = high level
 Blank = low level

Figure 2 - Schematic of Ruggedness Test

TABLE 9

ANALYSIS OF VARIANCE OF RUGGEDNESS TEST

<u>Variable</u>	<u>d.f.</u>	<u>M.S.</u>	<u>F-Test^{b/}</u>	<u>F-Test^{c/}</u>	<u>Contribution^{d/} to Total Variance (%)</u>	<u>Cumulative Variance (%)</u>
A	1	539.64	345.02	129.41	19.2	19.2
O	1	475.79	304.20	114.10	16.9	36.1
F	1	384.71	245.97	92.26	13.7	49.8
J	1	236.89	151.46	56.81	8.4	58.2
H	1	210.45	134.55	50.47	7.5	65.7
E	1	192.32	122.96	46.12	6.8	72.5
C	1	159.35	101.88	38.21	5.7	78.2
G	1	136.93	87.54	32.84	4.9	83.1
B	1	130.30	83.31	31.25	4.6	87.7
K	1	107.47	68.71	25.77	3.8	91.5
D	1	92.80	59.33	22.25	3.3	94.8
I	1	66.72	42.66	16.00	2.4	97.2
Q	1	34.96	22.35	8.38	1.2	98.4
L	1	14.39	9.20	3.45	0.5	98.9
P	1	9.24	5.90	2.22	0.3	99.2
M	1	6.44	4.12	1.54	0.2	99.4
N	1	5.88	3.76	1.41	0.2	99.6
S	1	4.17	2.67	-	0.1	99.7
(dummy)						
R ^{a/}	1	4.09	2.61	0.98	0.1	99.8
e ⁻	320	1.56	-	-	-	-

a/ Based on the replicate analyses.

b/ Using the replicate residual.

c/ Using the dummy residual.

d/ Ignoring the e term, which is of trivial size, anyway.

The "replicate residual" and the "dummy residual" are both used for completeness. Fortunately, the two residuals are not very different in size. Therefore, it appears plausible to claim that interactions among the real variables are not present to any large extent.

For convenience, in Table 9 the variables are listed in decreasing order of importance. Regardless of which column of F-values is "best," the contribution to the total variance is the statistical criterion for evaluating the significance of the variables.

Table 9 shows that the three variables A, O, and F account for half of all the variability in the MTB method. The first seven variables account for almost four-fifths of the variability in the data, and every variable below accounts for less than 5%. Probably the first 7 or 10 variables on the list are the only ones with a practical significance as far as the MTB method is concerned. Unfortunately, this is still a rather long list.

Although the primary objective of the ruggedness test is to decide which variables are important, the actual magnitude of the effects is also important. The ruggedness test analysis directly examines the difference in bias between high and low sulfate levels, i.e., labels a variable significant if and only if the variation in bias is larger. It is also desirable to examine the magnitude of the bias (without reference to changes in bias between levels). Table 10 illustrates both quantities. For example, variable A is significant in the statistical analysis because $2.20 - (-0.80) = 3.00$ is a large change in bias. However, the average (positive) bias is also worth noting, i.e., the average calculated value is significantly less than the average sample value. The ruggedness test shows that all of the variables examined will produce analytical results that are high (positive bias). No single variable produced a large effect. However, the combined effect of a change in the flow rates (i.e., the quantity of each reagent delivered) could be substantial. This change would most likely be observed as a change in sensitivity. Since standards are analyzed before, during, and after each analysis, a change in sensitivity should have a minimal affect on the accuracy of the determination. One of the inherent advantages of an automated analysis is the capacity to run numerous standards during the analysis so that the response of the system is well defined for a given period.

On the other hand, a substantial loss in sensitivity will have a more serious affect on the accuracy of the method. Therefore, it is important that near nominal flow rates be maintained.

TABLE 10

VARIABLE EFFECTS IN SULFATE ANALYSIS

<u>Variable</u>	<u>Average Response^{a/} ($\mu\text{g/ml}$)</u>	<u>Average Response^{a/} ($\mu\text{g/ml}$)</u>	<u>Δ ($\mu\text{g/ml}$)</u>	<u>Average Bias of Variable (%)^{b/}</u>
A	2.20	-0.80	3.00	5.45
O	2.11	-0.70	2.81	5.11
F	1.97	-0.56	2.53	4.60
J	1.70	-0.29	1.99	3.62
H	-0.23	1.64	1.87	3.40
E	-0.19	1.60	1.79	3.25
C	-0.11	1.52	1.63	2.96
G	-0.05	1.46	1.51	2.75
B	1.44	-0.03	1.47	2.67
K	0.04	1.37	1.33	2.42
D	0.08	1.33	1.25	2.27
I	1.23	0.18	1.05	1.91
Q	0.32	1.09	0.77	1.40
L	0.95	0.46	0.49	0.89
P	0.51	0.90	0.39	0.71
M	0.54	0.87	0.33	0.60
N	0.55	0.86	0.31	0.56
S	0.57	0.84	0.27	0.49
R	0.57	0.84	0.27	0.49

a/ Response in sample value/calculated value.

b/ Calculated from $(\Delta \cdot 100/2) \div$ average sulfate level.

Although the basic flow rates are controlled by the automated equipment and are beyond the control of the analyst, some components of the system can affect the overall performance. Checks should therefore be made of these components. These components include the pump tubing which should be checked when installed and frequently thereafter to establish that the proper delivery rates are being maintained. Pump tubing should be replaced at periodic intervals and whenever the delivery rate changes. The pump should be well maintained, the system should be frequently checked for restriction in the flow lines and the ion exchange column, and proper functioning of the pulse suppressors. The reagents should also be carefully prepared since concentration changes will affect the quantity of reagent delivered to the system, a change which is essentially the same as a change in flow rates.

Other than the above considerations, the only other significant variable was the interference produced by the phosphate ion. Currently this is related to the composition of the sample and is beyond the control of the analyst.

III. METHOD STRENGTHENING

The method write-up originally submitted has been rewritten to incorporate editorial and technical comments. The results of the ruggedness test were then used to strengthen the method weakness when possible. This tentative final method write-up of the methylthymol blue procedure is attached as an appendix.

The largest contributing actor was the NaOH concentration (final pH). The specification on the NaOH concentration was not changed but the flow rate of all reagent lines was modified to increase the delivery precision. A frequent check on the flow rates was also included. This general method strengthening should correct variables A, F, J, H, E, C, G, B, K, D, and I or the 11 most significant functions with the exception of the phosphate interference. The improvement obtained in the method by these modifications has not been evaluated.

It may be possible to remove the phosphate interferences using lanthanum salts as recommended by Palaty,^{14/} calcium or zinc salts as recommended by Belcher^{16/} and Jones.^{17/} The applicability of these procedures to the MTB method was not evaluated during this program. The remaining six functions produce a variance of 2.6%. There is no solution apparent to further correct function Q (color and turbidity) and P (cations). The function L (analysis temperature) has been controlled by a change in the method write-up.

The function M (MTB age) is resolved in the method by the instruction "make fresh daily."

We have not corrected the write-up for N (wash/sample time) or R (sample concentration). The effect of both of these functions are small-- 0.2 and 0.1% variance. The decision not to strengthen the method for these two functions was made on the basis of optimization. The effect of sample concentration (0.1%) could be eliminated by limiting the method to a range of 5 to 30 $\mu\text{g/ml}$. It is believed that the minor improvement obtainable does not justify such a severe range limitation.

The sampled wash ratio was investigated further after the ruggedness test. An improvement can be obtained by going to a 20 sample/hr cam with a 72-sec sample time and a 108-sec wash time. This timing arrangement appears to be near the optimum for the system. However, a decrease in the analysis rate of 10 samples/hr is probably not justified for a gain of only 0.2% variance.

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APPENDIX

TENTATIVE METHOD FOR THE DETERMINATION OF
SULFATES IN THE ATMOSPHERE (AUTOMATED
METHYLTHYMOL BLUE PROCEDURE)

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Tentative Method for the Determination of
Sulfates in the Atmosphere (Automated
Methylthymol Blue Procedure)^{a/}

^{a/} A tentative method is one which has been carefully drafted from available experimental information, reviewed editorially within the Methods Standardization Branch and has undergone extensive laboratory evaluation. The method is still under investigation and therefore, is subject to revision.

1. Principle and Applicability

1.1 Ambient sulfates are collected by drawing air through a glass fiber filter with a high-volume pump. The filters are extracted with water and the extract is treated with barium chloride and methylthymol blue at a pH of 2.8. After the barium sulfate precipitates, the pH is increased to 12.4 and the unreacted barium forms a chelate with the MTB. The uncomplexed MTB remaining is then measured colorimetrically at 460 nm.

1.2 The method is applicable to the collection of 24-hr samples in the field and subsequent analysis in the laboratory.

2. Range and Sensitivity

2.1 The range of the analysis is 5 to 60 $\mu\text{g SO}_4^-/\text{ml}$. With a 50-ml extract from 1/12 of the high volume filter collected at a sampling rate of 1.7 M^3/minute (60 cfm) for 24 hr, the range of the method is 1 to 12 $\mu\text{g}/\text{M}^3$. The lower range may be extended up to 12-fold by increasing the portion of the filter extracted. The upper limit may be increased by diluting the sample with distilled water.

2.2 Using the procedure outlined, a concentration of 5 $\mu\text{g SO}_4^-/\text{ml}$ will produce a scale deflection of 1.6% of full scale (signal/noise ratio of 2).

3. Interferences

3.1 Sulfides, sulfites, and phosphates produce a positive interference which is dependent on the concentration of sulfate and the interfering ion.

3.2 The interferences from cations are eliminated by passing the sample through an ion-exchange column.

4. Precision and Accuracy

4.1 The relative standard deviations for sampling $\text{SO}_4^{=}$ concentrations of 30 and 60 $\mu\text{g}/\text{M}^3$ are 2 and 1%, respectively.

4.2 The accuracy of the method in the range of 0 to 10 $\mu\text{g}/\text{M}^3$ is -5.8%; 10 to 20 $\mu\text{g}/\text{M}^3$ is -5.7%; 20 to 40 $\mu\text{g}/\text{M}^3$ is -2.5%, and over 40 $\mu\text{g}/\text{M}^3$ is -8.7%.

5. Apparatus

5.1 Sampling: Apparatus as specified in "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36 (84): 8191-8194, April 30, 1971, shall be used.

5.2 Analysis

5.2.1 Automatic Analyzer: An automated analytical system must be used for the determination of water soluble sulfate by this method. Alkaline solutions of methylthymol blue decompose on exposure to air. The method therefore cannot be adapted to a manual procedure. The automated system consists of the following components:

5.2.1.1 Sample Turntable: With a 30 sample/hr cam having a 1:2 sample to wash time ratio.

5.2.1.2 Proportioning Pump: Capable of supplying independently variable flow rates in eight supply lines.

5.2.1.3 Mixing Coils: Three small 14-loop (7.5 cm long) mixing coils.

5.2.1.4 Pulse Suppressors: Two pulse suppressors are required, one on the methylthymol blue line and one on the sodium hydroxide line as shown in Figure 1.

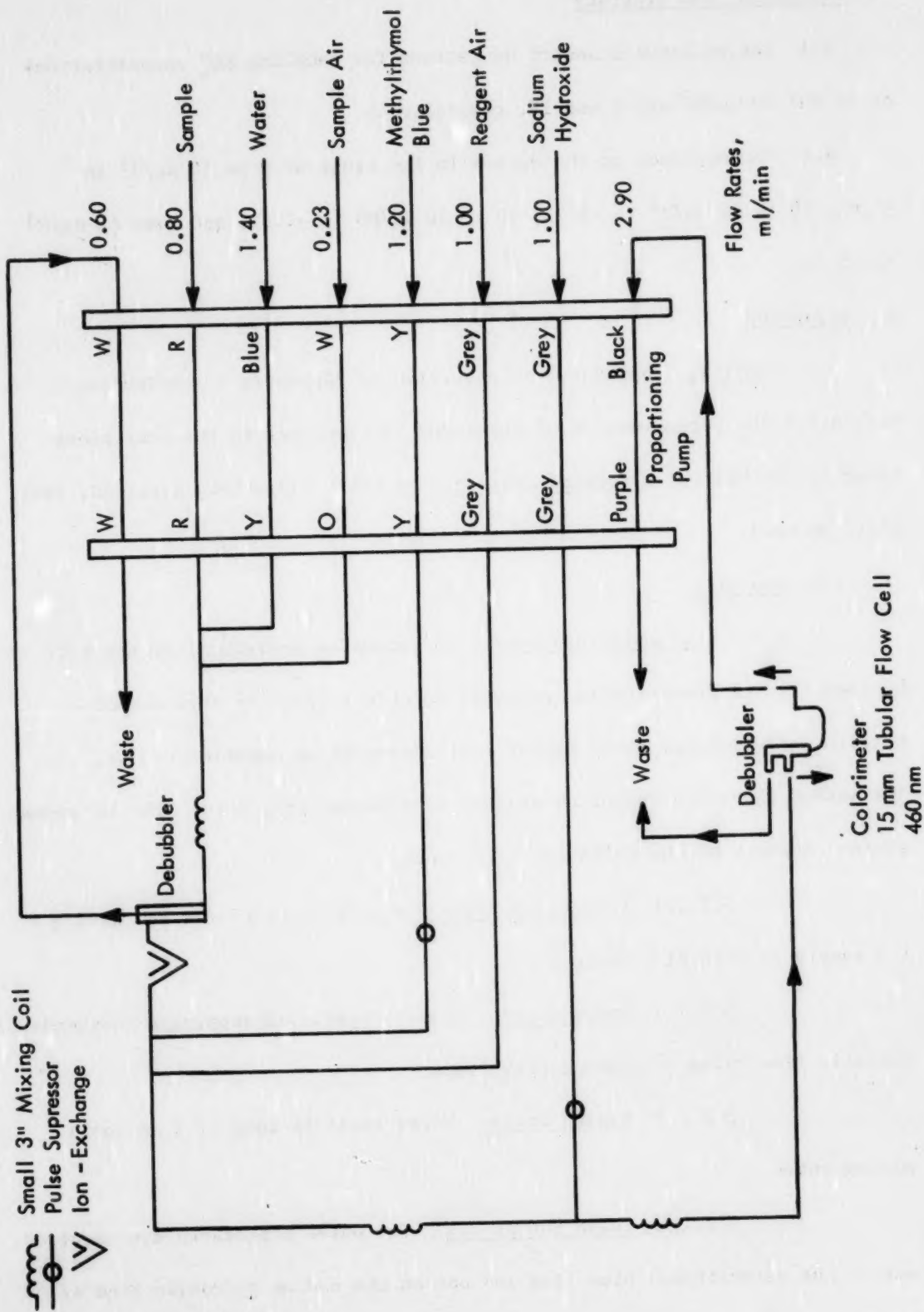


Figure 1 - Analytical Flow Diagram

5.2.1.5 Ion-Exchange Column: Interfering heavy metals are removed by the use of an ion-exchange resin. Use Dowex 50W-X8, sodium form, 300-850 μm (20-50 mesh). The resin should be stirred into distilled water and the fines discarded before they can settle. The resin should be soaked before use, at least overnight, and may be stored under distilled water until used. To pack a column, a small piece of glass wool is inserted in one end of a piece of plastic tubing 10 cm (4 in) long and 2.3 mm (0.09 in) I.D. A rubber pipet bulb is attached to the end of the tubing containing the glass wool plug. The other end of the tubing is placed in the soaked resin container and the rubber bulb operated until the tubing is filled with resin. The column must be free of trapped air after filling with resin. The resin column should be replaced after a full day's use.

5.2.1.6 15 mm Flow Cell Colorimeter: A stable colorimeter suitable for use at 460 nm with a band width of no greater than 18 nm at half height. Wavelength accuracy should be checked prior to use and quarterly thereafter.

5.2.1.7 Recorder: Strip chart recorder or digital printer matched to the colorimeter output.

5.2.1.8 Pump Tubing: Flow rated tubing of the capacities shown in Figure 1.

5.2.2 Sonic Cleaner: Of suitable size to process the required number of samples and at least 7.6 cm (3 in) deep.

5.2.3 Volumetric Flasks: 100, 200, 500, 1,000 ml capacity.

5.2.4 Pipets: 4, 5, 7, 10, 20, 25, 50-ml volumetric; 10 ml graduated in 1/10 ml intervals.

- 5.2.5 Pyrex Glass Wool
- 5.2.6 Plastic Tubing: 10 cm (3.94 in) and 2.3 mm (0.09 in) I.D.
- 5.2.7 Rubber Pipet Bulb
- 5.2.8 Buchner Funnels: Buchner style 150 ml capacity with fine-pore fritted glass filter.

5.2.9 Vacuum Filtering Apparatus: Device which permits vacuum filtering directly into the receiver. This consists of a bell jar with a top opening, a side tubulation and a bottom plate. The Buchner funnel passes through the top opening and is sealed to the bell jar with a stopper. The bell jar should be tall enough to contain the polyethylene bottles used for storing the samples. The vacuum connection is made using the side tubulation. The filtering apparatus is shown in Figure 2.

5.2.10 Vacuum Pump: Any device which can maintain a vacuum of at least 64 cm of Hg. Mechanical pumps or water aspirators may be used.

5.2.11 Polyethylene Bottles: Bottles with a capacity of 60 ml (2 oz) fitted with polyseal caps.

5.2.12 Glass Bottles (clear): 60 ml (2 fl oz) glass bottles with polyseal caps.

5.2.13 Glass Bottles (brown): 500 ml glass bottles with polyseal caps.

5.2.14 Graduated Cylinder: 10-ml capacity.

6. Reagents

6.1 Sampling

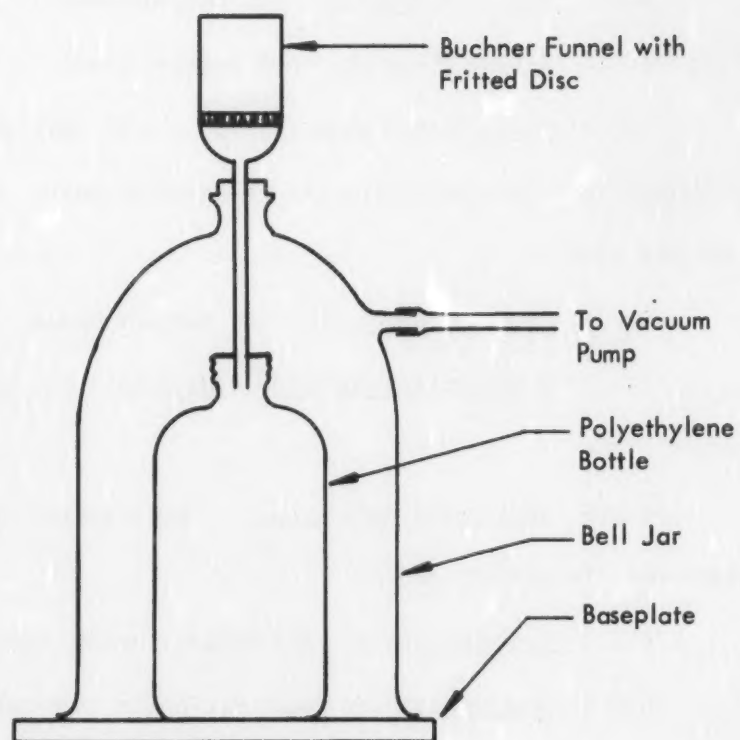


Figure 2 - Vacuum Filtering Apparatus

6.1.1 Filter Media: Filter media as specified in "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36 (84): 8191-8184, April 30, 1971, shall be used. Each lot of filters should be analyzed for sulfate and those producing a blank value > 1 µg/ml should be rejected.

6.2 Analysis

6.2.1 Sodium Hydroxide: ACS Reagent Grade.

6.2.2 Barium Chloride: ACS Reagent Grade.

6.2.3 Methylthymol Blue (MTB): 3', 3''-Bis[N,N-Bis (Carboxymethyl) Amino] Methyl Thymolsulfone-phthalein Pentasodium salt. 96% minimum by spectro analysis.

6.2.4 Ammonium Chloride: ACS Reagent Grade.

6.2.5 Concentrated Ammonium Hydroxide: ACS Reagent Grade, 28-30% NH₃.

6.2.6 EDTA Tetra Sodium Salt: Tetra sodium ethylenediamine Tetraacetate, Technical Grade.

6.2.7 Sodium Sulfate: ACS Reagent Grade, anhydrous.

6.2.8 Concentrated Hydrochloric Acid: ACS Reagent Grade, 36.5-38% HCl.

6.2.9 Ethanol: USP, 95%.

6.2.10 Sodium Hydroxide Solution (0.15 N): Dissolve 4.0 g of sodium hydroxide in distilled water and make to 500 ml in a volumetric flask.

6.2.11 Hydrochloric Acid Solution (1.0 N): Add 8.3 ml of concentrated hydrochloric acid to water in a volumetric flask and make to 100 ml.

6.2.12 Barium Chloride Solution (0.006 M): Dissolve 1.466 g of barium chloride dihydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) in distilled water and make to 1,000 ml in a volumetric flask.

6.2.13 Methylthymol Blue Solution: To 0.1301 g of MTB in a 500-ml volumetric flask add successively 25 ml of barium chloride solution, 4 ml of 1.0 N hydrochloric acid, and make to 500 ml with 95% ethanol. Prepare fresh daily, and store in a brown glass bottle.

6.2.14 Buffer pH 10.1: Dissolve 6.75 g of ammonium chloride (NH_4Cl) in 500 ml of distilled water. Add 57 ml of concentrated ammonium hydroxide (NH_4OH) and dilute to 1,000 ml with distilled water. Adjust the pH to 10.1 with additional NH_4OH .

6.2.15 Buffered EDTA (wash solution): Dissolve 40 g of tetrasodium EDTA in pH 10.1 buffer solution and make to 1,000 ml with additional buffer solution.

6.2.16 Stock Sulfate Solution (1,000 $\mu\text{g SO}_4^{2-}/\text{ml}$): Dissolve 1.4789 g of sodium sulfate (Na_2SO_4), which has been heated at 105°C for 4 hr and cooled in a dessicator over anhydrous magnesium perchlorate, and dilute to 1,000 ml with distilled water. Store under refrigeration.

6.2.17 Blank Reagent Solution: In a 500 ml volumetric flask add successively 25 ml of barium chloride solution, 4 ml of 1.0 N hydrochloric acid, and make to 500 ml with 95% ethanol.

7. Procedure

7.1 Sampling: Sampling procedures as specified in "Appendix B - Reference Method for the Determination of Suspended Particulate in the Atmosphere (High Volume Method)," Federal Register, 36 (84): 8191-8194 (30 April 1971), shall be used.

7.2 Analysis

7.2.1 Sample Extraction: The filters are removed from the folder, opened flat, and cut into 1.9 by 20.3 cm (3/4 x 8 in) strips using a paper cutter. The filter should be cut with the particulates face up. One or more filter strips are placed in a 60 ml (2 oz) glass bottle. Fifty milliliters of distilled water is pipetted into each bottle which is then closed with a polyseal cap. The samples are placed in the sonic bath, which should be refilled with fresh cold tap water to the level of the liquid in the bottles for each set of extractions. The sonic bath is operated for 30 minutes. The extracts are immediately vacuum filtered using the Buchner funnels and the vacuum filtering apparatus. The samples are filtered directly into polyethylene bottles. The filters should not be washed or squeezed, and the filtrates are not diluted. After filtering is complete, the polyethylene bottles are capped with polyseal caps and stored upright until analyzed.

7.2.2 Sample Analysis: An automatic analyzer is employed for analysis. A flow diagram and reagent flow rates are shown in Figure 1. The absorbance is measured at 460 nm and a flow cell with a path length of 15 mm is employed. The sample turntable rate is 30 samples per hour with a 1:2 sample to wash time ratio. The elapsed time between sample pickup and the corresponding peak is approximately 6 minutes. The instrument should be zeroed and spanned following the manufacturers directions.

The automatic analyzer is operated at the beginning of each day, after a fresh ion-exchange column is installed and prior to the first sample analysis, until a drift free baseline is obtained. This normally requires a

minimum of 2 hr. This is a convenient period in which to run several series of standards (see 8.2). When a stable baseline is obtained, a final series of standards should be run. A blank filter strip sample should be inserted with this set of standards. This will establish the blank absorbance data required to calculate the final values. Analysis should be conducted in a laboratory with reasonable temperature control since the method is moderately temperature sensitive.

Approximately 10 ml of each sample to be analyzed should be transferred to a sample cup and placed in the turntable. Every tenth sample cup should contain a 30 $\mu\text{g SO}_4^{\text{m}}/\text{ml}$ standard. A second set of standards should be run half way through the analysis. The baseline will remain noisy throughout the day with some peak tailing. Peak height should be measured perpendicular to the baseline to the highest part of the peak. Samples which exceed the absorbance of the highest standard of the calibration curve (60 $\mu\text{g SO}_4^{\text{m}}/\text{ml}$) are diluted until the concentration falls within the calibration range. When operating the automatic analyzer, air bubbles should not be allowed to enter the ion-exchange column. If air bubbles become trapped, the ion-exchange column should be replaced with a new column. A broadening of the colorimeter output with a corresponding loss in peak height usually indicates a performance decay in the pump tubing. At the first indication of peak broadening, the pump tubing should be replaced. The use of silicon rubber tubing in place of the standard pump tubing is highly recommended. Standard pump tubing should be replaced every day if used. Other available tubing has correspondingly longer life (~ 3 weeks) with silicon rubber tubing

having performed satisfactorily for as long as 5 weeks. If a plasticized tubing is used, it should be washed with acetone followed by distilled water prior to its use.

If the extracts are highly colored or contain suspended particulate, a blank must be run on the samples. This may be accomplished by replacing the MTB solution (6.2.12) with blank reagent solution (6.2.16) and performing the analysis for a second time. The absorbance values from the sample blanks should then be used in calculating the final sulfate concentration.

At the end of each day of analysis, a third series of standards should be run, including a filter blank. A random 5-10% of the samples should be rerun throughout the day to maintain internal quality assurance.

After completing the final analysis, the system should be cleaned with the EDTA solution. With the analyzer operating, place the MTB line and the NaOH line in distilled water for 2-3 minutes. Then transfer the MTB and NaOH lines to the EDTA solution container for 10 minutes. All liquid lines are then finally washed with distilled water for 15 minutes before shutting down the analyzer. The sample line may be conveniently washed during this operation by shutting off the turntable when the sample probe is in the wash position. All liquid lines should be left filled with water after the system has been washed. A coating will slowly develop on the internal parts of the flow system. When the coating becomes noticeable, the mixing coils should be cleaned by pumping 1N ammonium hydroxide through the system. The rate at which the coating develops is variable depending on

the nature of the samples being analyzed. A coating will slowly build up on the flow cell windows which is not removed by the NH_4OH wash. This build up is indicated by a loss in colorimeter sensitivity and may be corrected by washing the cell with 1N HCl followed by an acetone and then a water wash.

8. Calibration

8.1 High Volume Sampler: The high volume air sampler shall be calibrated as specified in "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36 (84): 8191-8194, April 30, 1971.

8.2 Automatic Analyzer

8.2.1 Flow Rates: The flow rates in the automatic analyzer system should be checked when the system is originally set up and once a week thereafter. It should also be checked when any systems substitutions are made. Disconnect the specific line, as it leaves the pump, and insert the line in a 10 ml graduated cylinder. Operate the pump for 2 minutes. If the flow rate is in error by more than 5%, change the pump tubing and recheck the flow.

The flow rates indicated in Figure 1 will produce the recommended reagent ratios. Minor variation in flow can be tolerated as long as they are constant since they will be corrected for in the calibration procedure.

8.2.2 Colorimeter Wavelength: The uncomplexed MTB at a pH of 12.4 has a maximum absorbance at 460 nm. If the colorimeter is of the interference filter type, the wavelength accuracy should be checked prior to use and quarterly thereafter. Maximum transmission of the filter should occur at 460 ± 15 nm. During the accuracy check, the filter must be mounted perpendicular to the light beam. Nonperpendicular mounting will produce an apparent

shift in the wavelength. If a colorimeter (spectrophotometer) with a prism or grating is used, the accuracy of the wavelength scale should be checked with a reference standard or by determining the indicated wavelength of minimum absorbance in the 460 nm area. This should be done under static conditions (pump shut off) with the cell containing a MTB solution (6.2.13) at a pH of 12.4.

8.2.3 Concentration Standards: Dilute 50.0 ml of stock sulfate solution containing 1,000 $\mu\text{g SO}_4^{=}$ /ml to 500 ml with distilled water. This intermediate sulfate solution contains 100.0 $\mu\text{g SO}_4^{=}$ /ml. Pipet 5, 10, 10, 15, 20, 50, and 60 ml of the 100 $\mu\text{g SO}_4^{=}$ /ml solution into 100, 100, 50, 50, 100, and 100 ml volumetric flasks and dilute to the mark with distilled water. The solutions contain 5, 10, 20, 30, 40, 50, and 60 $\mu\text{g SO}_4^{=}$ /ml, respectively.

8.2.4 Calibration Curve: The absorbance of the reaction products does not conform to Beer's Law. The plot of peak height versus concentration is hyperbolic rather than linear - a hyperbolic curve is expressed by $Y = X/(A + BX)$. If Y equals peak height in millimeters and X equals the sulfate concentration in micrograms per milliliters; typical values will be for A: 0.3 to 0.4, and for B: 5×10^{-4} to 1.5×10^{-3} .

Three series of standards are run each day: one at the beginning of analysis (after system is stable), one at the midpoint of analysis, and one after the final analysis. Each of the three standard series are subjected to a least squares hyperbolic curve fit. The average values for A and B from the first and second standard series are used to calculate concentrations from unknown peak heights for analysis performed during this

period. The peak heights for the 30 $\mu\text{g SO}_4^-/\text{ml}$ samples analyzed with the unknowns in which the 30 μg standard fails to agree should be rerun. The same procedure should be applied to the second half of the analysis using the second and third series of standards.

8.2.5 Frequency of Calibration: The calibration should be performed daily following the procedure outlined in 8.2.4.

9. Calculations

9.1 High Volume Sampler: Calculations relating to the high volume sampler shall be done in accordance with "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36(84):8191-8194, April 30, 1971.

9.2 Calculate Constants A and B

$$Y = X/(A + BX)$$

where A and B = Constants

Y = Peak height of standard, mm

X = Conc. of standard, SO_4^-/ml

9.3 Sulfate Concentration: Calculate concentration of $\text{SO}_4^- \mu\text{g/ml}$ using values for constants A and B obtained in 9.2.

$$X = \frac{AY}{1 - BY}$$

where A and B = Constants

Y = Peak height of unknown, mm

X = Conc. $\text{SO}_4^- \mu\text{g/ml}$

9.4 Calculate Total $\mu\text{g SO}_4^{\equiv}$ Collected

$$T = \frac{X V_1 W_f}{W_s}$$

where

T = Total $\mu\text{g SO}_4^{\equiv}$ collected, μg

X = Concentration of sample from 9.4, $\mu\text{g/ml}$

V_1 = Volume of extraction liquid, ml (normally 50 ml)

W_f = Width of exposed filter, cm (normally 20.3 cm)

W_s = Width of Sample analyzed, cm (normally 1.9 cm)

9.5 Calculate Concentration of Ambient Sulfates

$$C = \frac{T}{V}$$

where

C = Concentration of ambient sulfates, $\mu\text{g/m}^3$

T = Total $\mu\text{g SO}_4^{\equiv}$, μg from 9.5

V = Total volume sampled, m^3 from 9.2.2 of "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36(84): 8191-8194, April 30, 1971.

10. References

- 10.1 "Appendix B - Reference Method for the Determination of Suspended Particulates in the Atmosphere (High Volume Method)," Federal Register, 36(84):8191-8194, April 30, 1971.
- 10.2 Lazrus, A. L., K. C. Hill, and J. P. Lodge, "A New Colorimetric Microdetermination of Sulfate Ion," Presented at the Technicon Symposium, "Automation in Analytical Chemistry," New York, New York, September 8, 1965.
- 10.3 Prince, J. F., "A Comparison Study of Glass Fiber Filter Extraction Technique," unpublished EPA report, February 1975.